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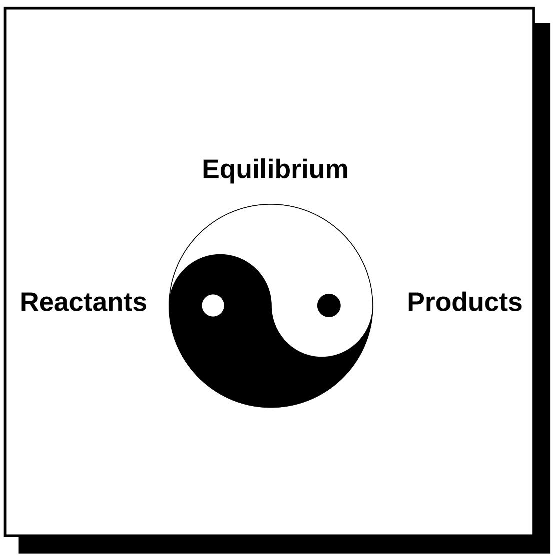

ChemSource

Instructional Resources for Preservice and Inservice Chemistry Teachers

CHEMICAL EQUILIBRIUM

Topic Overview

Content in a Nutshell

Up to this point, chemical reactions have likely been presented to students as being either "complete" or having "no reaction." As a consequence, it is probably not surprising that students are puzzled by chemical reactions where constant amounts of reactants and products are present simultaneously. This phenomenon is because chemical reactions can be reversible. Consider the reaction between nitrogen oxide and ozone represented by the equation:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

Using a simple collision theory model of reaction, NO and O_3 molecules can collide, rearrange their atoms, and form NO_2 and O_2 molecules as products. But if this is so, why can't NO_2 and O_2 molecules collide and reform NO and O_3 molecules? The answer is that they can; the reaction is probably better represented by the equation

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

The rate at which NO_2 and O_2 form varies because of the changing concentrations of NO and O_3 as they are used up while being converted to NO_2 and O_2. The same is true for the reverse reaction. Eventually, the rates of the forward and reverse reactions become the same, and the consequence is a state of "balance" or "equilibrium" among the amounts of NO, O_3, NO_2, and O_2 present. Although the reaction appears to have ceased on the macroscopic scale, the forward and reverse reactions continue at the molecular level. This is a "dynamic" equilibrium in contrast to a "static" equilibrium as represented, for example, by a balanced see-saw.

Several examples of dynamic equilibria (as physical changes) may already befamiliar to your students. When water evaporates in a closed container, a constant "vapor pressure" is reached. This pressure is exerted by the water vapor molecules when the rate of evaporation is equal to the rate of condensation. Also, in the dissolving of asolid in a liquid solvent, a limit is reached where no more solid will dissolve. This saturation point is reached when the rate of dissolution is equal to the rate of crystallization.

In quantitative terms, chemists are interested in the position of equilibrium, *i.e.*, to what extent the reaction has approached completion when the equilibrium state is reached (*i.e.*, is the reaction 90% complete, 60% complete?). The extent of completion for chemical reactions varies with different reactions. It is usually expressed as the ratio of concentrations of products to reactants (which is theoretically a constant value, K, at a fixed temperature). Specifically, for the hypothetical reaction: a A + b B $\rightleftharpoons$ c C + d D, where capital letters represent reactants and products and lowercase letters represent coefficients:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Place in the Curriculum

The position of an equilibrium can be shifted toward reactants or products according to LeChatelier's principle (a stress placed on a system at equilibrium will cause a shift that minimizes the stress). Factors (stresses) that influence chemical equilibrium positions are those that affect the rates of forward reactions differently from the rates of reverse reactions. The principal factors are concentration effects and temperature effects. Pressure effects are often included in this list, but the idealgas law shows that pressure can only be changed by changing concentration (concentration is equal to n/V; consequently any changes in amount of gas or volume of gas will change the concentration), or by changing the temperature.

Equilibrium is usually considered a "later" topic in first-year chemistry. When it is taught, there are three different levels to approaching the content: (1) limiting instruction to descriptive or qualitative issues (LeChatelier's principle), (2) interpreting values of K (*e.g.*, weak *vs.* strong acids), and (3) a complete quantitative approach (calculating values of K). The focus of this module is on the qualitative level of equilibrium, leaving quantitative aspects to *Extensions and Projects*.

CENTRAL CONCEPTS

1. The products of a chemical reaction can often react and reform the reactants (reversibility).
2. A chemical system can reach a state of dynamic balance between its forward and reverse reactions. This state is called chemical equilibrium.
3. A stress placed on a system at equilibrium will cause a shift that minimizes the stress (LeChatelier's Principle).
4. The concentrations of reactants and products in a chemical system at equilibrium are related mathematically (Law of Mass Action; the equilibrium constant).

RELATED CONCEPTS

1. **Gases (Gas Laws)** The general gas law describes the relationship among the variables P, T, V, n. Relationships often described in textbooks as Boyle's Law, Gay-Lussac's Law, Charles' Law, and Avogadro's Law are usefully regarded as subsets of the general gas law.
2. **Rates of Reactions (Kinetics)**
   a. The rate of a chemical reaction can be changed by varying the experimental parameters (T, P, concentration, surface area, catalyst, substance).
   b. The collision theory of reaction rates qualitatively explains the factors affecting reaction rates.
3. **Solutions and Stoichiometry** Stoichiometry in solutions is conveniently based on attention to the molar concentrations (M) of reacting species. A chemical equation is the basis for interpreting and predicting quantitative relationships in chemical reactions (stoichiometry). Stoichiometric relationships are based on the mole concept.
4. **Acids and Bases** Strong electrolytes (acids, bases, salts) dissociate completely in solution. By contrast, weak electrolytes dissociate only slightly.
5. **Thermochemistry** A reaction that releases heat is termed an exothermic reaction. If the reaction absorbs heat, it is called an endothermic reaction.

RELATED SKILLS

1. **Chemical Skills**

   Write balanced net ionic equations.
   Write formulas of molecules, ions, radicals, and complexes.
2. **Mathematical Skills**

   Complete basic stoichiometric calculations.
   Use molar concentration units.
3. **Laboratory Skills**

   Use acid/base indicators.

Performance Objectives

After completing their study of equilibrium, students should be able to:

1. state the conditions that result in some reactions reaching equilibrium while others do not.
2. predict the direction of shift in a system at chemical equilibrium, given a change in concentration, temperature, or pressure.
3. describe equilibrium and equilibrium shifts on the molecular level.
4. write the equilibrium expression for a system at chemical equilibrium.
5. calculate a value for K for a system at chemical equilibrium from suitable concentration data.
6. calculate the concentration of a reactant or product in a chemical equilibrium given the value of K, and all other reactant and product concentrations at equilibrium.

Concept/Skills Development

LABORATORY ACTIVITY: STUDENT VERSION

Activity 1: Concentration Effects

Introduction

In this laboratory activity you will investigate chemical reactions of the type $A + B \rightarrow C$. You will then add several reagents to the reaction mixture to see the effect of each on the reaction.

Purpose

This laboratory activity will help you gain an understanding of a new type of chemical reaction.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. Dispose of the chemicals as your teacher directs.

Procedure

1. Place about 50 mL 0.005 M KSCN, potassium thiocyanate, solution in a 100-mL beaker. Note the appearance of the solution.
2. Add about five drops 0.2 M $Fe(NO_3)_3$, iron(III) nitrate, solution to the KSCN solution and stir. Make notes about the appearance of the $Fe(NO_3)_3$ solution and of the combined solutions.
3. Fill each of five test-tubes about one-third full of the solution prepared in Step 2. Label one test-tube as the "standard" and place it in your test-tube rack.
4. In a second test-tube, put one drop of the $Fe(NO_3)_3$ solution. Mix and observe any changes that occur. Write your observations.
5. In the third test-tube, put a few crystals of solid KSCN (about the size of a small pea). Mix gently while observing and record your observations.
6. In the fourth test-tube, put one drop 0.1 M $AgNO_3$, silver nitrate solution. Mix and observe any changes that occur. Write your observations.
7. In the fifth test-tube, put a few crystals of solid NaF, sodium fluoride (about the size of a rice grain). Mix gently while observing and record your observations.
8. Thoroughly wash your hands before leaving the laboratory.

Data Analysis and Concept Development

1. Write comparisons of the solutions in the five test-tubes.
2. Potassium ions (K^+) and nitrate ions (NO_3^-) are not active in any of the chemical reactions of this activity. Such "inactive" ions are sometimes termed "spectator ions." They are present because they are carried along with the "active" part of the chemical involved in the reaction. What are the active substances in the reaction between $Fe(NO_3)_3$ and KSCN?
3. The product of this reaction is $FeSCN^{2+}$. Write a balanced equation for the reaction studied in this laboratory activity.

4. What evidence is there for a chemical reaction between $Fe(NO_3)_3$ and KSCN?
5. Identify the cause of the color of the solution formed in Step 2.
6. Why does the color change when one drop of $Fe(NO_3)_3$ solution is added to the solution formed in Step 2?
7. Why does the color change when solid KSCN is added to the solution formed in Step 2?
8. What is the cause of the changes observed when the $AgNO_3$ solution is added? Write an equation to represent these changes.
9. Why does the color change when solid NaF is added to the solution?

Implications and Applications

Ammonia gas, NH_3, can be formed by the reaction of hydrogen gas, H_2, and nitrogen gas, N_2. The formation of ammonia is exothermic. An equilibrium is established according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

Predict the effects of each of the following on the equilibrium system. (Does the equilibrium shift to the right, to the left, or remain unchanged?)

1. Adding more nitrogen gas or hydrogen gas at constant volume and temperature.
2. Removing some ammonia gas at constant volume and temperature.
3. Heating the system at constant volume.
4. Decreasing the pressure of the system by changing the volume of the reaction vessel at constant temperature.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 1: Concentration Effects

Major Chemical Concept

This is intended as an introductory activity involving the concept of dynamic equilibrium. The ideas developed in this activity are: (1) chemical reactions do not always go to completion, and (2) a state of dynamic equilibrium can be established in a chemical system by the simultaneous formation of products from reactants and reactants from products. Dynamic equilibrium does not necessarily (or usually) occur when equal concentrations of reactants and products exist in the chemical system.

Level

While the laboratory activity itself is quite easily performed, the underlying notions are not basic level concepts. The activity fits well in either a general or honors level course.

Expected Student Background

1. Familiarity with observational evidence for chemical reactions.
2. Knowledge of common ions and ionic representations of equations.
3. Experience with double replacement reactions.
4. Some knowledge of kinetic molecular theory.

Time

Completing the activity and answering questions requires one 50-min class period.

Safety

No safety precautions beyond those that apply to normal chemical laboratory work need to be stressed for this activity. Some students may be concerned with the superficial resemblance between SCN^- and CN^-. Although SCN^- should be treated with the same respect as other chemicals, it does not have the level of toxicity of CN^-. Soluble chemicals should be washed down the drain with plenty of water. Solid chemicals should be disposed of in a solid waste jar.

Materials (For 24 students working in pairs)

60 Test-tubes, 18- x 150-mm
12 Test-tube racks
12 Beakers, 100-mL
12 Medicine droppers
0.2 M Iron(III) nitrate, $Fe(NO_3)_3$, small dropping bottle
0.005 M Potassium thiocyanate, KSCN, 50 mL
Potassium thiocyanate, KSCN, solid, 5 g
0.1 M Silver nitrate, $AgNO_3$, small dropper bottle
Sodium fluoride, NaF, solid, 5 g

Advance Preparation

$Fe(NO_3)_3$ solution 8 g solid $Fe(NO_3)_3 \cdot 9H_2O$ in 100 mL solution. Carefully add 2-3 drops of concentrated nitric acid, HNO_3, to the solution. (*NOTE: The acid stabilizes the solution and represses the formation of a yellow color.*)

KSCN solution 0.05 g solid KSCN in 100 mL solution. Include enough concentrated nitric acid (a few drops) to make the solution slightly acidic. (*NOTE: This solution may not keep. Check the solution before using.*)

$AgNO_3$ solution 1.7 g solid $AgNO_3$ in 100 mL solution.

Small, centrally located containers of solid KSCN and NaF will be sufficient.

Pre-Laboratory Discussion

Students should be told that although the procedure is short and relatively simple, their detailed observations are essential in answering the questions and in understanding the concept being studied. No procedural instructions are needed except the location of the solutions and the solid KSCN.

Teacher-Student Interaction

While students are performing the activity, walk around the laboratory correcting errant procedures, and asking students for oral interpretations of their observations. This is not the time to explain the observations to students. Your questioning serves to focus students' thoughts on the system being observed. Assure students that there will be a class discussion of this laboratory activity after they have finished it.

Anticipated Student Results

The colorless KSCN solution and nearly colorless $Fe(NO_3)_3$ solution should form a brownish-red product. Adding either $Fe(NO_3)_3$ solution or KSCN crystals deepens the color of the solution. Adding $AgNO_3$ or NaF causes the color of the solution to fade.

Answers to Data Analysis and Concept Development

1. Students will write their observations in making the comparisons. General consensus should be obtained during the class discussion.
2. The active species are Fe^{3+} and SCN^-.
3. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$ (*NOTE: Students will probably not know to include the double arrow. This symbol can be introduced at the appropriate time in the post-laboratory discussion.*)
4. The evidence for a chemical reaction between $Fe(NO_3)_3$ and KSCN is the observed color change.
5. Some $FeSCN^{2+}$ product forms when $Fe(NO_3)_3$ solution is added to the KSCN solution. Although the $Fe(NO_3)_3$ solution may have been slightly colored, the deep color of the mixture of $Fe(NO_3)_3$ and KSCN solutions cannot be explained by dilution of $Fe(NO_3)_3$ solution with the colorless KSCN solution.
6. The color change is caused by the production of more $FeSCN^{2+}$. Formation of more $FeSCN^{2+}$ indicates that SCN^- was still available in the solution to react with Fe^{3+} from $Fe(NO_3)_3$.
7. The color changes when KSCN solid is added because SCN^- from the KSCN reacts with Fe^{3+} still present in the system. *(NOTE: The importance of the answers to Questions 5 and 6 is that neither reactant—Fe^{3+} or SCN^-—had been completely used up in forming product during the original mixing of the solutions. This key set of observations can serve as the focal point for introduction of the idea of dynamic equilibrium.)*

8. Two observations will be noted. First, Ag^+ reacts with SCN^- to form the precipitate AgSCN, decreasing the SCN^- concentration and shifting the equilibrium to the left. The second observation is the fading of the solution color as $FeSCN^{2+}$ concentration decreases. Focus class discussion on the fading color and its meaning. *(NOTE: The specific role of Ag^+ can be demonstrated by adding enough $AgNO_3$ to make the solution colorless, filtering the solution, and testing separate samples of filtrate with Fe^{3+} and SCN^-. The color should return with SCN^-, but not with Fe^{3+}, thus showing that Ag^+ removed SCN^-.) Students can be led to this conclusion by questions, trial, and error.*
9. As in Question 8, the color fades, indicating a decrease in $FeSCN^{2+}$ concentration. The evidence from the laboratory is that the F^- reacts with and removes the Fe^{3+}. This is the result of F^- forming a complex with Fe^{3+} to form FeF_6^{3-}. Focus on the meaning of the observable evidence in the class discussion. *(NOTE: Questions 8 and 9 can be used to develop the idea of reversibility of chemical reactions and the role of concentration in controlling reactions.)*

Answers to Implications and Applications

1. a. Shift the equilibrium toward products
   b. Shift the equilibrium toward products
   c. Shift the equilibrium toward reactants
   d. Shift the equilibrium toward reactants

Post-Laboratory Activities

Part B of *Laboratory Activity 2: Temperature Effects* can be combined with this activity if there is enough time. If this activity is done, tell students to save any excess solution made in Procedure 2 to use in *Laboratory Activity 2*.

After students have had time to prepare answers to the questions, lead a class discussion on the laboratory activity. In this discussion it is important to establish first that all student groups have compatible observations of the systems. Discuss any discrepant observations through questioning to clear up any problems. If students are adamant about observations that differ, do a quick demonstration to gain consensus.

Students may suggest that the reaction is a double displacement (*aka.*, double replacement or metathesis) reaction between potassium thiocyanate and iron(III) nitrate, according to: $3KSCN + Fe(NO_3)_3 \rightarrow Fe(SCN)_3 + 3\ KNO_3$. However, both products suggested by this equation would be soluble and ionic, resulting in identical ionic reactants and products (show this using a net ionic equation); thus such a prediction would not, by itself, account for the observations. If a precipitate had formed, there would be an argument in favor of the double displacement reaction. Of course, some sort of chemical reaction *did* occur as documented by the color change.

The formation of the complex ion $FeSCN^{2+}$ may cause some difficulty for students. It could be explained that the Fe^{3+} ion attracts the SCN^- ion strongly enough to hold them together as an ion. Actually, the chemical reaction is not the important focus of the activity. In fact, this laboratory activity could be carried out equally well by labeling the reactants as 'A' and 'B' and the colored product as 'C'. All of the same logic can be used to develop the ideas of the activity.

A discussion of the chemistry of the reaction can be done by using the questions as a discussion outline. As stated earlier, answers to Questions 6 and 7 permit you to suggest to students that it is possible for a chemical reaction to occur so that the final system contains *all* reactants and products simultaneously.

Pose a question about whether it is reasonable to accept the idea that products (in this reaction the product is $FeSCN^{2+}$) could change chemically back to reactants, as well as reactants changing chemically to form products. If students agree to such a possibility, ask them to offer an explanation for such a phenomenon. When a satisfactory explanation has been obtained, you can insert the double arrow in the chemical equation and explain that it designates to chemists that the system is reversible, that is, that it contains all reacting species.

Student laboratory observations can be used to establish the idea that this constantly changing system (on the molecular level) is still able to achieve constant concentrations of reactants and products (as observed by the constancy of the colors of the solutions).

The darkening of the solution when more of either reactant is added can be used (either now or later) as an example of LeChatelier's principle. You may decide that this is the best place to introduce the idea of LeChatelier's principle, or it might be better to address this principle after completing *Laboratory Activity 2* (see *Extensions*).

Extensions

1. Temperature effects on equilibrium point of a system (see *Laboratory Activity 2*).
2. Pressure effects on the equilibrium point of a gaseous system.

Assessing Laboratory Learning

Questions

1. Sodium chloride, NaCl, has a solubility of approximately 36 g/100 mL water. If 45 g of NaCl were added to 100 mL of water, 36 g would dissolve as Na^+ and Cl^- ions, but 9 g of solid NaCl would remain. Explain how this system could involve a dynamic equilibrium between solid NaCl and dissolved ions. *[Because the water molecules and dissolved ions are in constant motion, Na^+ and Cl^- ions could deposit on the NaCl solid, but for every pair of ions depositing on the solid, another pair of ions would go from the solid to the dissolved state.]*
2. What effect would adding 5 mL of KNO_3 solution to your "standard" test-tube (see Step 3) have on the test-tube solution's color? Note that a water solution of KNO_3 is colorless. *[The color of the "standard" solution would be less intense, due to dilution, but added KNO_3 would not cause a chemical change. It contains K^+ and NO_3^- ions that were "spectators" in the reaction.]*
3. Explain why an open beaker with zinc metal, Zn, and hydrochloric acid, HCl, will not establish chemical equilibrium. The products of the reaction of zinc metal and hydrochloric acid are hydrogen gas, H_2, and zinc chloride, $ZnCl_2$, solution. *[The system will not achieve equilibrium because a product—hydrogen gas—leaves the system. In order for dynamic equilibrium to be established, all products and reactants must remain in the system.]*

LABORATORY ACTIVITY: STUDENT VERSION

Activity 2: Temperature Effects

Introduction

In this laboratory activity you will study two chemical systems and observe the effect of temperature changes on them: (1) the aqueous ammonia system and (2) the Fe^{3+}/SCN^{-} system first studied in *Laboratory Activity 1*.

Purpose

To determine the effect of temperature on chemical systems.

Safety

1. Wear protective goggles throughout the laboratory activity.
2. *CAUTION: The test-tube will be hot after heating. Be sure to use a test-tube holder.*
3. Concentrated ammonia solution has a strong odor. Avoid breathing the ammonia fumes. Be careful not to spill any concentrated ammonia solution on yourself. If you do spill any, wash the area with large amounts of water and notify your teacher.
4. Dispose of the chemicals as your teacher directs.

Procedure

Part A

1. Place about 400 mL distilled water in a large beaker.
2. Add one drop concentrated ammonia solution. Stir well.
3. Fill two large test-tubes half full of this solution.
4. Add one drop phenolphthalein indicator to each test-tube. The solution should be pink, but not dark pink (see teacher-made solution for exact color).
5. Gently heat one of the test-tubes over a burner until the solution begins to boil. Reserve the other test-tube as a “standard” for comparison. Record your observation of any changes that occur. Compare the heated solution with that of the unheated “standard” solution.
6. Let the tube cool for a few seconds, then place it in a stream of cold water. Record any changes that occur.

Part B

1. Put about 50 mL 0.005 M KSCN, potassium thiocyanate, solution in a 100-mL beaker. Note the appearance of the solution.
2. Add about five drops 0.2 M $Fe(NO_3)_3$, iron(III) nitrate, solution to the KSCN solution and stir. Make notes about the appearance of the $Fe(NO_3)_3$ solution and the combined solution.
3. Fill each of three test-tubes about one-third full of the solution made in Step 2. Label one test-tube as the “standard” and place it in your test-tube rack.
4. Place one of the test-tubes in a boiling water bath for 5 min. Place a second test-tube in a salt-ice water bath for 5 min. Compare the solution in each bath with your “standard” solution at room temperature.
5. Thoroughly wash your hands before leaving the laboratory.

Data Analysis And Concept Development

1. What ion accounts for the pink color of the aqueous ammonia solution?
2. Write a chemical equation for the reaction between ammonia and water resulting in the ion identified in Question 1.
3. What evidence is there that a chemical change occurred when the test-tube was heated? Write a chemical equation for this chemical change.
4. What effect did cooling the solution have on the aqueous ammonia solution? Write a chemical equation for this chemical change.
5. Is the reaction involved in Question 4 exothermic or endothermic? How do you know?
6. Write a net ionic equation for the reaction between iron(III) nitrate and potassium thiocyanate.
7. Analyze the equation you wrote in Question 6 in a manner similar to that of the aqueous ammonia system and determine whether this reaction is exothermic or endothermic.
8. Generalize about the effect of heat on reversible chemical reactions.

Implications and Applications

1. Why would the aqueous ammonia reaction not work well if too much ammonia were added?
2. Discuss how a change in temperature of a liquid solvent affects the solubility of a solid solute.

LABORATORY ACTIVITY: TEACHER NOTES

Activity 2: Temperature Effects

Major Chemical Concepts

This activity is designed to develop the concept that a change in temperature can affect the equilibrium position of a chemical system.

Level

Basic, general or honors students

Expected Student Background

General knowledge of solutions and concentrations, formula writing, equation writing, balancing equations, effect of indicators in a solution, and acids and bases in solution.

Time

One 50-min for the laboratory activity and the discussion in which the concept is developed from the observations.

Safety

See safety suggestions in *Student Version*.

Materials (For 24 students working in pairs)

12 Beakers, 600-mL
36 Beakers, 100-mL
12 Burners
12 Test-tube holders
48 Test-tubes, 18- x 150-mm
12 Test-tube racks
12 Medicine droppers

Consumables (For 24 students working in pairs)

Phenolphthalein, in dropper bottle
Concentrated NH_3, ammonia, small dropper bottle (in Procedure A, two drops of dilute NH_3 can be used.)
Ice
0.2 M Iron(III) nitrate, $Fe(NO_3)_3$, small dropper bottle (see *Activity 1*)
0.005 M Potassium thiocyanate, KSCN, 60 mL (see *Activity 1*)

Advance Preparation

It is advisable to prepare a solution of the concentrated ammonia and phenolphthalein, that shows the desired color. Display the desired color of the solution to students before they start the laboratory procedure. Directions for preparation of the other solutions are in *Laboratory Activity 1*.

Pre-Laboratory Discussion

A discussion of the effect of indicators in basic and acidic solutions may be helpful to students. You may want to do *Part A*, Steps 1-3, as a class demonstration, and then make the excess ammonia solution available to students to complete the rest of the activity.

Teacher-Student Interaction

During the laboratory activity, it is advisable to move from group to group to insure that students have obtained the desired color with the phenolphthalein indicator. Have students look down the tube for a better color comparison. Make sure they do not look down the tube while heating it.

When students have gathered the data, have them attempt to write a chemical equation for what happened. They can be led to this equation by answering the questions in the activity. Many students, however, may need the class discussion to develop the equation unless they learned about the interaction of acids with water in previous acid-base studies.

Anticipated Student Results

The pink color of the aqueous ammonia solution should disappear when the solution is heated. The pink color returns when the solution is cooled. The color of $FeSCN^{2+}$ fades as the solution is heated. Cooling reverses this effect.

Answers to Data Analysis and Concept Development

1. The phenolphthalein is an indicator for base. The pink color indicates the presence of hydroxide ion in the solution.
2. The water hydrolyzes the ammonia according to the equation:

   $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

   Students will probably not indicate the reaction as an equilibrium until reversibility is established in later questions.
3. The fading of pink color indicates a decrease in hydroxide ion concentration. This evidence for the disappearance of a reactant indicates a chemical reaction. The reaction is the reverse of the reaction of Question 2:

   $$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$
4. The re-emergence of the pink color indicates an increase in hydroxide ion concentration. It also establishes this reaction as reversible (equilibrium):

   $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
5. Exothermic. Heat is absorbed by the products to reform reactants and thus shift the reaction to the left. This is consistent with what is observed:

   $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) + \text{Heat}$$
6. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$ (See discussion for *Laboratory Activity 1*.)
7. The reaction is exothermic. Since the color (due to the product $FeSCN^{2+}$) fades when the solution is heated, heat is absorbed by the product as the reaction shifts to the left:

   $$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq) + \text{Heat}$$
8. Heat can shift the equilibrium position by being absorbed by reactants (if the reaction is endothermic) or products (if the reaction is exothermic), causing the added heat to be partially consumed in the reaction.

Answers to Implications and Applications

1. If the ammonia concentration is too high, the added heat may not lower the hydroxide ion concentration enough to change the color due to phenolphthalein.

2. As a rule of thumb, increasing the temperature of a solid/liquid mixture will increase the solubility of the solid. This is true because most dissolution processes of solids in water are endothermic. (There are exceptions. Increasing the temperature of a gas/liquid solution will decrease the solubility of the gas because the entropy factor is much more important in gaseous systems.)

Post-Laboratory Discussion

Use the "Data Analysis and Concept Development" questions as the basis of a discussion to develop the ideas of temperature effects on systems at equilibrium.

Extensions

1. Have students predict the effect that cooling would have on a system at equilibrium. After predictions are made, perform a laboratory activity in which the solution is cooled.
2. Possible Laboratory Activity: Boil 200 mL cold, saturated $CoCl_2$(aq), cobalt(II) chloride solution. The cherry red solution turns blue. Pour the solution into a 15- x 60-mm test-tube. Place the lower quarter in salt-ice bath and heat the upper portion. The lower end becomes red, while the upper portion becomes blue (see *Demonstration 2*).

Assessing Laboratory Learning

Questions

1. What is a reversible reaction? *[A reaction where products can recombine to form reactants.]*
2. Compare the rates of forward and reverse reactions for a chemical system at equilibrium. *[Forward rate = Reverse rate]*
3. How is chemical equilibrium related to a reversible reaction? *[A reversible reaction is an example of chemical equilibrium.]*
4. What is chemical equilibrium? *[Behavior of a chemical reaction where forward and reverse reactions proceed at the same rate.]*
5. Using Le Chatelier's Principle, explain the effect of adding heat to a system at equilibrium. *[The system will respond by favoring the reaction that counteracts the heat increase; the endothermic reaction predominates.]*
6. Present a demonstration in which an equilibrium is shifted due to a change in temperature. Have students write an equation for the reaction, and explain the shift in equilibrium [*e.g.*, *Demonstration 1* based on $2NO_2(g) \rightleftharpoons N_2O_4(g)$].

DEMONSTRATIONS

Demonstration 1: $2NO_2(g) \rightleftharpoons N_2O_4(g)$ and Temperature

Purpose

To demonstrate the effect of temperature on a system at equilibrium.

Materials

Hot water bath
Ice water bath
3 NO_2(g)-filled tubes
Dry ice/acetone bath (optional)
Overhead projector

Safety

No special precautions are necessary other than those given in the directions.

Procedure

Obtain NO_2/N_2O_4 (nitrogen dioxide/dinitrogen tetroxide) gas tubes from an educational scientific supply house (*e.g.* ,Temperature Equilibrium Tubes, Sargent-Welch #4426).

Place one tube into a beaker of hot water 70 to 80 °C, one tube into a beaker of ice water (alternative: a dry ice/acetone bath; it will turn the gas colorless), and leave one tube at room temperature. Place all three tubes on an overhead projector and ask students to make observations. Write the equilibrium equation on the board:

$$\underset{\text{Brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{Colorless}}{N_2O_4(g)} + \text{Heat}$$

Ask students to use LeChatelier's principle to account for their observations.

Demonstration 2: $2NO_2(g) \rightleftharpoons N_2O_4(g)$ and Pressure

Purpose

To demonstrate the effect of pressure on a system at equilibrium.

Materials

Glass syringes, 30-mL
Plastic syringe cap
Nitrogen dioxide, $NO_2(g)$

Safety

Care must be taken to contain the NO_2 gas, preventing it from escaping into the room.

Procedure

In a hood collect some NO_2 in a syringe (Cu + HNO_3 (conc.) produces NO_2) by air displacement. Seal the syringe with a plastic syringe cap so no gas can escape. Firmly and rapidly press on the syringe to compress the gas as much as possible. At first the NO_2 gas appears darker (increased concentration) and then should fade (equilibrium shift). Demonstrate this reaction for individual students or small groups, since it may be hard to see. Write the following equilibrium equation:

$$\underset{\text{Brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{Colorless}}{N_2O_4(g)}$$

Discuss how increased pressure should shift the equilibrium to the right, lessening the color.

Demonstration 3: Temperature Effects on Cobalt Complexes

Purpose

To demonstrate the effect of temperature on a system at equilibrium.

Materials

Cobalt(II) chloride hexahydrate, $CoCl_2{\cdot}6H_2O$, (9.5 g per 100 mL solution)
Concentrated HCl (hydrochloric acid), 100 mL
Hot plate
Ice water bath
3 Beakers, 250-mL

Safety

Since the solution is highly acidic it should be neutralized with sodium bicarbonate before disposal and flushed down the drain.

Procedure

Pour 100 mL $CoCl_2$ solution into a 250-mL beaker; add concentrated HCl until the solution changes color (pink to blue). This may take considerable HCl (about 100 mL). Divide the solution into three beakers. Place one on a hot plate, one in an ice bath, and the third at room temperature. Have students explain the colors in terms of the following equation:

$$\text{Heat} + [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

Demonstration 4: Rubber Band Equilibrium

Purpose

To demonstrate the effect of temperature on a physical equilibrium system.

Materials

Heavy rubber band
Hooked weights (100-500 grams depending on rubber band)
Ringstand and ring
Hair dryer
Meter stick

Safety

No special precautions are necessary.

Procedure

Suspend the weight from a rubber band attached to a ring stand. Put a meter stick next to the weight so that its distance from the table top can be measured. Discuss this system as an example of a physical system in static equilibrium. Ask students to predict what will happen if the rubber band is heated. Heat the rubber band with a hair dryer and measure its distance from the table. Allow it to cool and measure again.

Heated rubber band will be shorter than cooled rubber band due to entropy. Heating the system causes the ordered orientation of the molecules to become disordered. In the three dimensional system the rubber band becomes shorter.

Group and Discussion Activities

Counterintuitive Examples, Discrepant Events

1. In a way, equilibrium systems are themselves discrepant events. The presence of all reactants and products in a reaction vessel is not expected by students who have generally been exposed earlier only to reactions that “go to completion.”
2. Students sometimes get the idea that higher temperatures drive reactions towards completion. If dissolution is treated as an equilibrium (Solute + Solvent $\rightleftharpoons$ Solution), for example, increasing the temperature is thought to increase the concentration of the solution. Although this is most often true with solid/liquid combinations, there are exceptions (*e.g.*, Li_2SO_4). The solubility of NaCl is hardly affected by temperature at all. The solubility of a gas decreaseswith increased temperature. Opening a warm can of soda pop amplydemonstrates this fact (see also Demonstration 2 in *Solubility and Precipitation* module).
3. Solubility equilibria are an excellent chance to challenge student ideas about physical *vs.* chemical changes. Ask students if a reaction resulting in a precipitate is a physical or chemical change [$M^+(aq) + A^-(aq) \rightarrow MA(s)$]. Then ask if the dissolution of an ionic salt is a physical or chemical change [$MA(s) \rightarrow M^+(aq) + A^-(aq)$]. Then show them that both reactions can be represented as one equilibrium reaction.

Pictures in the Mind

These diagrams represent molecular activity during a reversible reaction. Figure 1 is just one example from the *Teacher's Resource Manual*, Concept Mastery section; *Chemistry: the Study of Matter* , Prentice-Hall, Dorin, Demmin, and Gabel, pp. CM-31 and 32. Have students label each drawing. Which drawing(s) represent the system at equilibrium (B and C) and which represent the system not at equilibrium (A and D)?

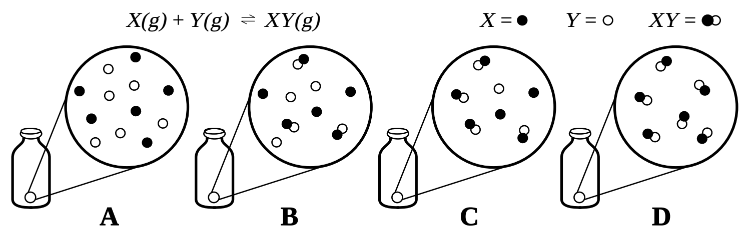

Figure 1. Pictures in the Mind.

Analogies and Metaphors

1. In a football game, the number of players on the field is constant although exchange of players (substitution) changes actual persons.
2. **Connected fish bowl analogy** Two fish tanks are connected by a tube large enough to allow passage of fish. A number of fish are placed in one of the tanks. At equilibrium, the number of fish in each tank will eventually become unchanged.
3. Two jugglers analogy.

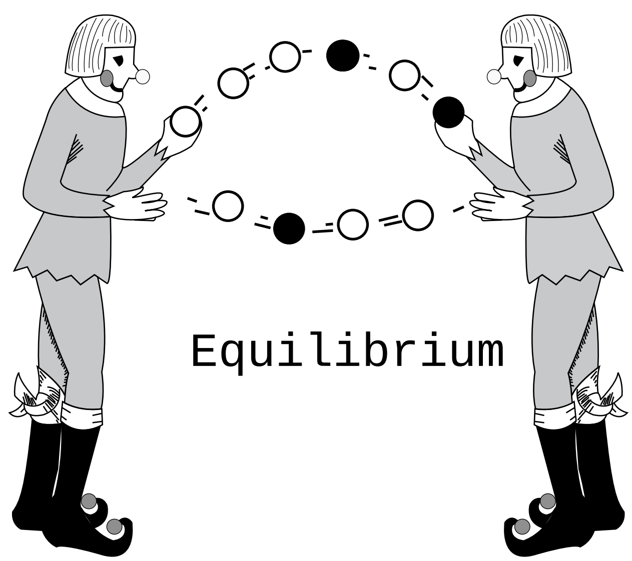

Figure 2. Two jugglers analogy.

4. Drinking fountain line:
   (a) Ten students waiting in line to get a drink of water on a hot day. As each gets a drink, the same student reenters the line (equilibrium in a closed system). (b) Same situation as "a," except as each student gets a drink and leaves, a new student enters the line (steady-state in an open system).
5. Picture a number of horses and wranglers in a corral. As each wrangler mounts a horse, the wrangler is bucked off. The equilibrium is:

   Horse + Wrangler $\rightleftharpoons$ Mounted wrangler

   Consider the effect (a la LeChatelier) of adding horses or wranglers.

Key Questions

1. Predict the direction of shift in a chemical equilibrium system given changes in concentration, temperature, and pressure. *[Answer this question by applying LeChatelier's Principle.]*
2. State the conditions that result in some reactions reaching equilibrium while others do not. *[All reactants and products of a chemical reaction must be present and in contact in order for an equilibrium state to be reached.]*
3. Describe equilibrium and equilibrium shifts at the molecular level.*[Use ideas of collision theory to answer this question.]*
4. Determine a value for *K* for a chemical equilibrium system from concentration data. *[See the discussion on Problem Solving in* Tips for the Teacher.*]*
5. Determine the concentration of a reactant or product in a chemical equilibrium system given the value of *K*. *[See a general chemistry text for the problem solving skills needed.]*
6. Determine the equilibrium expression for a chemical equilibrium equation. *[See the discussion on Problem Solving in this module.]*

Other

1. **Have students write essay answers to questions about Pictures in the Mind** (see examples in *Pictures in the Mind*).

   Examples of questions:

   a. Tell whether each picture represents a system in equilibrium.

   b. Explain your answer for each picture.

2. **Simulation** Have students set up a factory to produce ammonia according to the Haber Process (see *Industrial Inorganic Chemistry* module). Include following steps.

   a. Invent process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

   b. Develop ideal conditions (temperature and pressure).

   Raising the temperature favors the endothermic reaction (the reverse reaction) in which the rise in temperature is counteracted by the absorption of heat. Increasing the pressure favors the forward reaction in which four gas molecules are converted to two gas molecules.

   c. Develop how conditions will be met in the factory.

   Gases are compressed to high pressures; thus the yield of ammonia is increased even though high temperature is maintained to make the reaction come to equilibrium quickly. (At 500 °C, yield of ammonia increases from 0.1% to 47% if pressure is increased from 1 atm to 700 atm.)

   d. Invent need for a catalyst.

   A catalyst needs to be used to make the reaction fast enough.

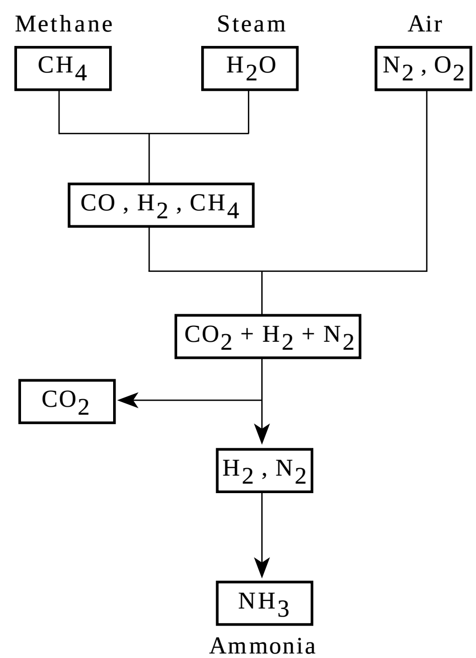

Figure 3. Steps of the Haber Process.

TIPS FOR THE TEACHER

Language of Chemistry

Key Words in LeChatelier's Principle

equilibrium the state of a chemical system in which the rate of product formation equals the rate of reactant formation.

stress refers to upsetting an established equilibrium system by adding more of a reactant or product to the system, or by changing reaction conditions such as temperature or pressure.

minimize means that a stressed equilibrium will respond to establish a new equilibrium state that reduces the added stress.

shift means that the adjustment of a stressed equilibrium system will result in the formation of more product (called a shift to the "right") or the formation of more reactant (called a shift to the "left").

Common Student Misconceptions

1. **"Reactions always go to completion."**

   The way we write chemical equations could imply that reactants completely become products. This is not necessarily true, especially in systems that establish equilibrium. The double reaction arrows $\rightleftharpoons$ serve to illustrate the fact that both reactants and products remain in a system at equilibrium.

2. **"Reactions at equilibrium have equal concentrations of reactants and products."**

   Actually, this is seldom the case at equilibrium. Values of equilibrium constants indicate the extent to which reactants form products. Large values represent reactions that go farther to the right before equilibrium is established.

3. **"Reactions at equilibrium have stoichiometrically related concentrations."**

   Some students think that the amounts of reactants and products in a reaction at equilibrium are fixed by the coefficients of the equation. The coefficients fix the relative amount that will react, not the amounts that are present.

4. **"Equilibria are static."**

   It is common for students to see chemical equilibrium as a static balance rather than a dynamic balance between forward and reverse interactions of molecules.

5. **"The right and left sides of an equation represent different regions of the reaction vessel."**

   A chemical equation is simply a formalized way to depict the chemical system, and the terms "left" and "right" refer *only* to the written equation. There is no "sidedness" to the chemical system itself. Reactants and products are intermingled.

Problem Solving

1. If equilibrium constants are calculated, skills associated with the mathematical solution of the problem need to be stressed.

Example: Given that $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, and that the molecular concentrations of reacting species at equilibrium were $[H_2] = 0.221$ M, $[I_2] = 0.221$ M, and [HI] = 1.563 M. Then:

$$K\text{eq} = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$K\text{eq} = \frac{(1.563\text{ mol/L})^2}{(0.221\text{ mol/L})(0.221\text{ mol/L})}$$

$$K_{\text{eq}} = 50$$

2. From a general problem solving point of view students will need to develop strategies for determining equilibrium shifts utilizing LeChatelier's Principle and changes in temperature, pressure and concentration.

$$K_{\text{eq}} = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

Addition of nitrogen gas, hydrogen gas, or ammonia gas to this system will cause shifts in the equilibrium. With heat on the right side of the equation, we see that the formation of ammonia is exothermic. Addition of heat to the system will cause a shift to the left. Increasing pressure on the system will cause a shift to the right because the smaller number of product particles would cause less pressure than the larger number of reactant particles, thus relieving the stress on the equilibrium caused by the increase in pressure.

3. Students are sometimes confused by shifts in equilibrium caused by temperature changes. If heat is represented as a product (in an exothermic reaction) or a reactant (in an endothermic reaction) in the equation for the reaction, then a change in temperature adds or takes away heat from the system. In this way, temperature is treated in the same way as increases or decreases in concentration. For example:

$$A + B \rightleftharpoons C + \text{Heat}$$

An increase in temperature increases the quantity of heat (a product), thus shifting the reaction to the left.

History: On the Human Side

1. **Fritz Haber and The Haber Process:** Fritz Haber, a German, received the Nobel Prize in chemistry in 1919 for synthesizing ammonia from its elements, nitrogen and hydrogen. Haber's life was filled with ironic tragedies. His motivation for developing a method for producing ammonia was to make possible unlimited supplies of fertilizer to replace the limited supply of natural fertilizers (from nitrate deposits in Chile). Many were predicting massive starvation in Europe unless this was done. Ironically, ammonia could also be used to produce explosives. As a result Germany was able to produce its own explosives during World War I despite a blockade of nitrate compounds by the Allied powers.

Haber was a patriot and German nationalist and as a consequence threw himself into the German war effort. One of his contributions was development of mustard gas, a horrible instrument of war that caused much suffering. Ironically, many compounds related to mustard gas have been use as anti-cancer agents, ultimately saving lives. The Nobel Prize he received was criticized by British, American, and French scientists.

A final irony in Haber's life occurred when he was driven out of Germany before World War II because of his Jewish ancestry, despite his proven loyalty to his country.

2. **Who was LeChatelier?** Henry Louis LeChatelier (1850-1936) was a French chemist who conducted research on chemical equilibrium, the combustion of gaseous mixtures on metals, alloys, *etc.* He enunciated his principle dealing with the equilibrium of a system as a result of study of the industrial production of iron. Iron oxides were heated with carbon monoxide in a blast furnace to produce iron and carbon dioxide. However, carbon monoxide was also found in the products. This puzzling finding was explained in various ways. After researching the problem, LeChatelier proposed the idea of a reversible reaction to account for the carbon monoxide.

HUMOR: ON THE FUN SIDE

1. Bumper Sticker (American Chemical Society, Office of Precollege Science, Room 806; 1155 Sixteenth Street, N.W., Washington, DC 20036)

   Old Chemists Never Die . . . . They Just Reach equilibrium
   Δ

2. Student response on exam:

   LeChatelier's Principle is, if a strain is applied on a substance, the substance will try to assume the most comfortable condition.

3. The meaning of "reversible reaction"? *Starting material recovered. (CHEM 13 NEWS, October 1970, p. 193)*

4. Word Search (see *Appendix* for master copy)

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C P R E R U S S E R P L R X I S Z
A N R X C S I X Y I R Y B A Z K X
A M M O N I A V R T N Y W I X M G
L S F T C D Q C K Z A F A U N U B
N N O H F Z G O G L U S T A T I C
R E V E R S I B I L I T Y I N R P
Y J J R R T S A U I X Y M L S B A
Z I A M T R O L C R C A S A M I E
U T P I N E S T X T X G I R N L C
Y D E C A S V I F V W R E K Z I E
B X W E R S S A T J E B I F W U P
H V F R F R M M K H A N J N J Q P
Z J R E I L E T A H C E L B I E L
```

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Change in the reaction conditions of an established equilibrium.

2. State of a chemical system such that the rates of formation of products and reactants are equal.
3. German chemist who synthesized Item 6 from nitrogen and hydrogen.
4. Characteristic of an equilibrium system.
5. Factor that can cause a shift in a gaseous system at chemical equilibrium.
6. Substance formed in the nitrogen plus hydrogen gaseous equilibrium.
7. Type of reaction in which heat is absorbed by products to reform reactants.
8. Metal in complex responsible for pink-to-blue color change as temperature changes.
9. Balanced see-saw represents this type of equilibrium.
10. French chemist for which a famous principle of equilibrium is named.

Answers: 1. STRESS 2. EQUILIBRIUM 3. HABER 4. REVERSIBILITY 5. PRESSURE 6. AMMONIA 7. EXOTHERMIC 8. COBALT 9. STATIC 10. LECHATELIER

5. See cartoons at end of module.

MEDIA

1. *Chemistry: Reaction Rates and Equilibrium*, 23 min. video available from Coronet/NTI Film and Video, 108 Wilmot Road, Deerfield, IL 60015; (800) 621-2131; (708) 940-3640 (FAX).
2. *Equilibrium*, CHEM Study film/video available from Ward's Natural Science Establishment, Inc., 5100 West Henrietta Road, P.O. Box 92912, Rochester, NY 14692-9012; (800) 2660.
3. *Introduction to Chemical Equilibrium*, Chem 101 Series, University of Illinois Visual Aids Service, 1325 South Oak, Champaign, IL 61820; (800) 367-3456.
4. Imperial Chemical Industries Ltd. *Laws of Disorder*, Pt 4: *Equilibrium: The Limit of Disorder*. ICI Film Library, Thames House North, Mill Bank London SW1P 40G. (Held at University of Minnesota, University Film & Video, 1313 Fifth St. SE, Minneapolis, MN 55414, 1-800-847-8241.)
5. TV Ontario: *Chemical Equilibrium*. Six 10-minute video programs with a guide covering various aspects of equilibrium. TVO Video, 143 West Franklin Street, Suite 206, Chapel Hill, NC 27516, 1-800-331-9566.
6. The *World of Chemistry* videotape "Number 14: Molecules in Motion." World of Chemistry Videocassettes. Annenberg/CPB Project, P.O. Box 1922, Santa Barbara, CA 93116-1922; (800) 532-7637; World of Chemistry Series, Atlantic Video, 150 South Gordon Street, Alexandria, VA 22304; (703) 823-2800 or QUEUE Educational Video, 338 Commerce Drive, Fairfield, CT 06430; (800) 232-2224. A secondary school version of this series is available from WINGS for Learning/SUNBURST, 101 Castleton Street, Pleasantville, NY 10570; (914) 747-3310; (800) 321-7511; (914) 747-4109 (FAX).

7. Software published by *JCE:* Software, a publication of the *Journal of Chemical Education*, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, Wl 53706-1396: (608) 262-5153 (voice) or (608) 262-0381 (FAX).

   a. *Equilibrium Calculator*, by Robert D. Allendoerfer. Vol. VI B, No. 1, for IBM PS/2 PC-compatible computers.

   b. *Equilibrium Calculator*, by Robert D. Allendoerfer. Vol. I D, No. 1, for Windows/IBM PC.

8. Software published by Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue. Madison, Wl 53706-1396: (608) 263-2837 (voice) or (608) 262-0381 (FAX).

   a. For the IBM PS/2 PC-compatible computer: PC 2901 (Equilibrium simulation program where user inputs data; concentration of each species after each given increment is given numerically or as bar graphs until equilibrium is reached.)

   b. For the Apple II computer: AP 603 (same as PC 2901).

9. Metcalfe, H., *et al.* (1986). *Modern chemistry: Disk for equilibrium chapter.* New York, NY: Holt, Rinehart, & Winston.

10. Prentice-Hall: *Dynamic Equilibrium*. 4343 Equity Drive, P.O. Box 2649, Columbus, OH 43216.

Links/Connections

Within Chemistry

1. Two of the most dangerous pollutants in the exhaust from automobiles are nitric oxide (NO) and carbon monoxide (CO). In the presence of a Monel (a nickel-copper alloy) catalyst, the concentrations of these gases are reduced by the following equilibrium process:

   $$2NO(g)\ 2CO(g) \rightleftharpoons N_2(g) + CO_2(g)$$

   The equilibrium constants vary with temperature as follows:

K_p	10^{98}	$10^{96.2}$	$10^{64.2}$	$10^{52.8}$	$10^{43.6}$
T(K)	600	700	800	900	1000

   Is the reaction exothermic or endothermic? *(Exothermic)*

2. A proposed method for collecting solar energy involves the equilibrium process:

   $$2SO_3(g) + \text{Heat} \rightleftharpoons 2SO_2(g) + O_2(g)$$

   The sulfur trioxide is heated in a chamber to 800 °C by solar energy. The sulfur dioxide and oxygen are then transported to a low-temperature heat exchanger where they recombine to form sulfur trioxide and liberate heat. At 800 °C, sulfur trioxide is 56% dissociated when the total pressure is 3.00 atm or 304 kPa. K_p is 1.05 atm or 1.07 X 10^5 Pa or 1.07 X 10^2 kPa.

3. K_{sp} (solubility product constant), K_a (dissociation constant for acids), K_b (dissociation constant for bases), and K_f (formation constant for species, such as $FeSCN^{2+}$ in this module's *Laboratory Activity 1*).

Between Chemistry and Other Disciplines

1. Chemical processing plants, such as oil refineries and chemical manufacturing plants, work with chemical reactions that establish dynamic equilibrium. It is often true that much creative energy is expended to determine how to shift the equilibrium so that the desired product is produced in large quantity and at a reasonable cost. A good example of this problem is the synthesis of ammonia from the elements, according to the equation:

   $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

2. Stalactite/stalagmite growth is based on equilibrium involving calcium carbonate and carbonic acid. See the article in *ChemMatters* by David Tanis (February 1984, pp. 10-11, "Underground Sculpture").

To the Contemporary World

Personal

1. The problem of the relationship between eating sugar and tooth decay should interest most students. Fermentation of sugar in the mouth involves an increase in H^+ concentration. Over a period of time, such as a night's sleep, increasing H^+ can shift the equilibrium between tooth enamel and the ions making up the enamel to the ion side of the reaction. The equilibrium is:

   $$\underset{\text{Tooth enamel}}{Ca_5(PO_4)_3OH(s)} \rightleftharpoons 5Ca^{2+}(aq) + OH^-(aq) + 3PO_4^{3-}(aq)$$

   Stress is put on this equilibrium by formation of HOH (H_2O) and/or HPO_4^{2-}, causing a net loss of solid enamel.

2. Carbon monoxide, a by-product of “incomplete” oxidation (burning) of hydrocarbons, poses a major pollution problem. It is dangerous to life because it binds to hemoglobin and therefore excludes oxygen. Hemoglobin is a complex molecule that transports oxygen in the blood system.

   The binding process can be represented by the equilibrium:

   $$\text{Hemoglobin} + O_2 \rightleftharpoons \text{Bound } O_2$$

   Because of a balance between the forward and reverse reactions, oxygen can be released where it is needed in the body. However, CO can also bind to hemoglobin:

   $$\text{Hemoglobin} + CO \rightleftharpoons \text{Bound CO}$$

   This equilibrium has a greater K_{eq} than the hemoglobin–O_2 reaction. Consequently the hemoglobin is not available to transport oxygen. The victim of CO poisoning suffocates.

3. Ozone in our upper atmosphere absorbs ultraviolet light from the sun according to the equilibrium:

   $$O_3(g) \overset{UV}{\rightleftharpoons} O_2(g) + O(g)$$

   The reverse action regenerates O_3, which can absorb more ultraviolet light. Chlorofluorocarbons have been used in aerosols and refrigerants. These substances can release chlorine radicals that destroy O_3 irreversibly. Scientists are concerned that increased levels of chlorofluorocarbons will migrate into the upper atmosphere and deplete the ozone supply, allowing larger quantities of potentially harmful ultraviolet radiation to penetrate to the earth’s surface.

Community

1. **Field trips** Control of equilibrium is a theme in many industrial processes. A visit to a local chemical industry might be a useful activity, although equilibrium probably should not be the only reason for the visit.
2. **Knowledgeable individuals** industrial chemists, university chemists, physicians, and pharmacists

Societal

A visit to a chemical plant to see the contrast between laboratory-based chemistry and scaled-up chemistry might be useful. Again, the direct association with equilibrium is not the sole reason for such a visit.

Extensions

1. **Relate equilibrium to solubility.** Partially soluble salts (*e.g.*, AgCl, PbI_2, or $PbCl_2$) can be used to explore the equilibrium aspects of solubility and to determine values for K_{sp}. Two approaches can be used. (1) Put a weighed excess of the salt in a measured amount of water; stir; filter the undissolved salt from the liquid, dry and weigh the undissolved salt. From the difference in masses the quantity of dissolved salt can be determined. (2) Precipitate the salt from soluble ions (*e.g.*, AgCl from $AgNO_3$ and NaCl). Filter the precipitate, dry and weigh. Compare the mass with the stoichiometrically expected mass. The difference is the mass of dissolved salt.
2. **Relate equilibrium to buffer action.** The pH of various buffered systems can be studied. The acetic acid/acetate system can be studied by varying the relative concentrations of the two species.
3. **Quantitative treatment of equilibrium.** Two straightforward methods can be used to derive equilibrium constants. (1) Measure the pH of a serial dilution of acetic acid from 0.1 M to 0.0001 M. Use a pH meter (inexpensive battery-operated ones can be obtained from Fisher Scientific – 13-300-51). (2) Compare the relative conductivity of 0.01 M HCl (assume 100% dissociation) with the same concentration of $HC_2H_3O_2$. By assuming the percent dissociation is related to the relative conductivity, the K_a value of acetic acid can be determined. An inexpensive battery-operated conductivity apparatus can be obtained from Fisher Scientific (09-331-4). It comes in two ranges and is called a dissolved solids tester. You may need two ranges to do this test (100-19,900 mS and 10-1,990 mS).

References

Module developed by Michael Abraham, Donna Coshow, and William Fix, the Oklahoma team.

Most college general chemistry texts thoroughly treat equilibrium. Various aspects of equilibrium include: general equilibrium, weak acid and base behavior, aqueous equilibrium (buffer solutions and solubility product), and dissociation (or formation) constants for complexes.

Davenport, D. (1985, February). When push comes to shove: Disturbing the equilibrium. *Chem Matters, 3*(1), 14-15.

This is a brief discussion of Le Chatelier's Principle.

Goran, M. H. (1967). *The story of Fritz Haber* . Norman, OK: University of Oklahoma Press.

Lund, E. W. (1968). Activated complex—a centenarian? A tribute to Leopold Pfaundler. *Journal of Chemical Education, 45,* 125.

An historical account of the ideas of a pioneer in equilibrium theory.

Oesper, R. E. (1931). The scientific career of Henry Louis LeChatelier. *Journal of Chemical Education, 8,* 442-461.

Parker, S. P. (Ed.). (1987). *McGraw-Hill encyclopedia of science and technology* (6th Ed.). New York, NY: McGraw-Hill.

This is a very good reference source for discussion information or student research information on many topics relating to equilibrium. This set is available in many schools and public libraries.

Runquist, E. A., and Runquist, O. (1972). Passage of fruit flies through a hole, a model for a reversible chemical reaction. *Journal of Chemical Education, 49,*534.

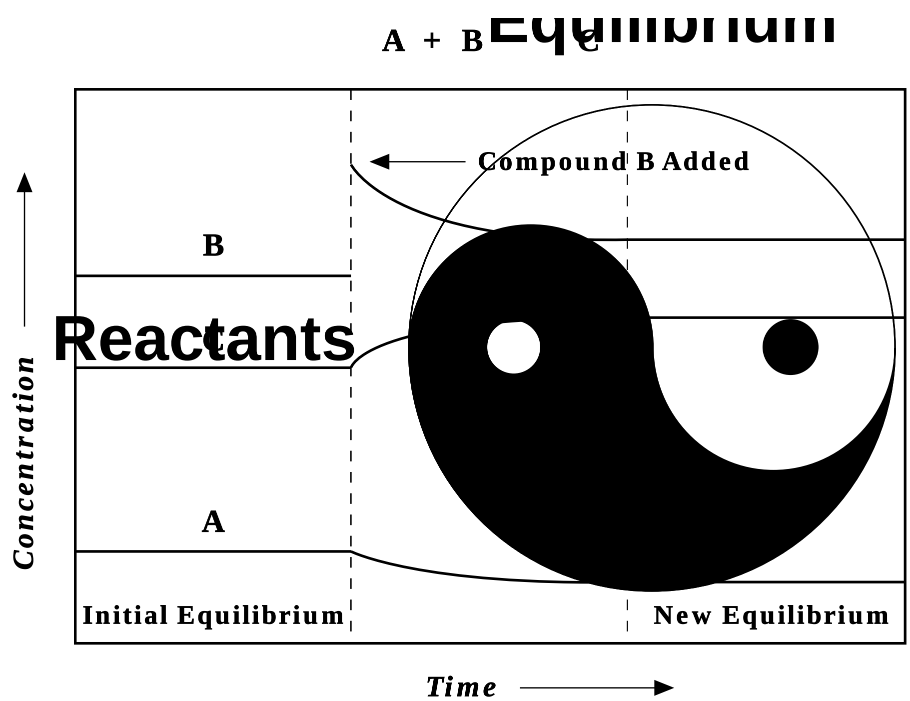
Slabaugh, W. H. (1967, November). Chemical equilibrium.*The Science Teacher, 34*(8), 61-66.

This is a brief discussion of equilibrium and how it is taught.

Appendix

- **Transparency Masters**
  1. Effect of Increasing Concentration on a Chemical Equilibrium System
  2. Word Search
- **Humor**

Effect of Increasing Concentration on a Chemical Equilibrium System

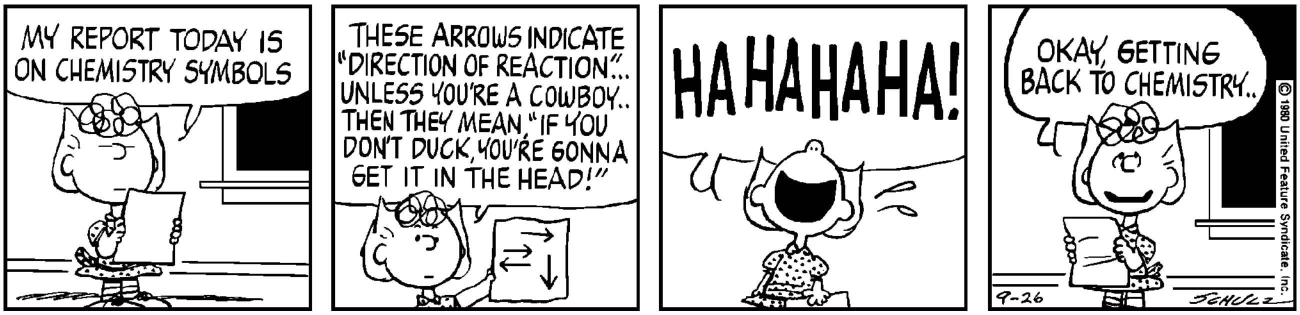


Word Search

C	P	R	E	R	U	S	S	E	R	P	L	R	X	I	S	Z
A	N	R	X	C	S	I	X	Y	I	R	Y	B	A	Z	K	X
A	M	M	O	N	I	A	V	R	T	N	Y	W	I	X	M	G
L	S	F	T	C	D	Q	C	K	Z	A	F	A	U	N	U	B
N	N	O	H	F	Z	G	O	G	L	U	S	T	A	T	I	C
R	E	V	E	R	S	I	B	I	L	I	T	Y	I	N	R	P
Y	J	J	R	R	T	S	A	U	I	X	Y	M	L	S	B	A
Z	I	A	M	T	R	O	L	C	R	C	A	S	A	M	I	E
U	T	P	I	N	E	S	T	X	T	X	G	I	R	N	L	C
Y	D	E	C	A	S	V	I	F	V	W	R	E	K	Z	I	E
B	X	W	E	R	S	S	A	T	J	E	B	I	F	W	U	P
H	V	F	R	F	R	M	M	K	H	A	N	J	N	J	Q	P
Z	J	R	E	I	L	E	T	A	H	C	E	L	B	I	E	L

Words about the concepts in this module can be obtained from the clues given. Find these words in the block of letters:

1. Change in the reaction conditions of an established equilibrium.
2. State of a chemical system such that the rates of formation of products and reactants are equal.
3. German chemist who synthesized Item 6 from nitrogen and hydrogen.
4. Characteristic of an equilibrium system.
5. Factor that can cause a shift in a gaseous system at chemical equilibrium.
6. Substance formed in the nitrogen plus hydrogen gaseous equilibrium.
7. Type of reaction in which heat is absorbed by products to reform reactants.
8. Metal in complex responsible for pink-to-blue color change as temperature changes.
9. Balanced see-saw represents this type of equilibrium.
10. French chemist for which a famous principle of equilibrium is named.



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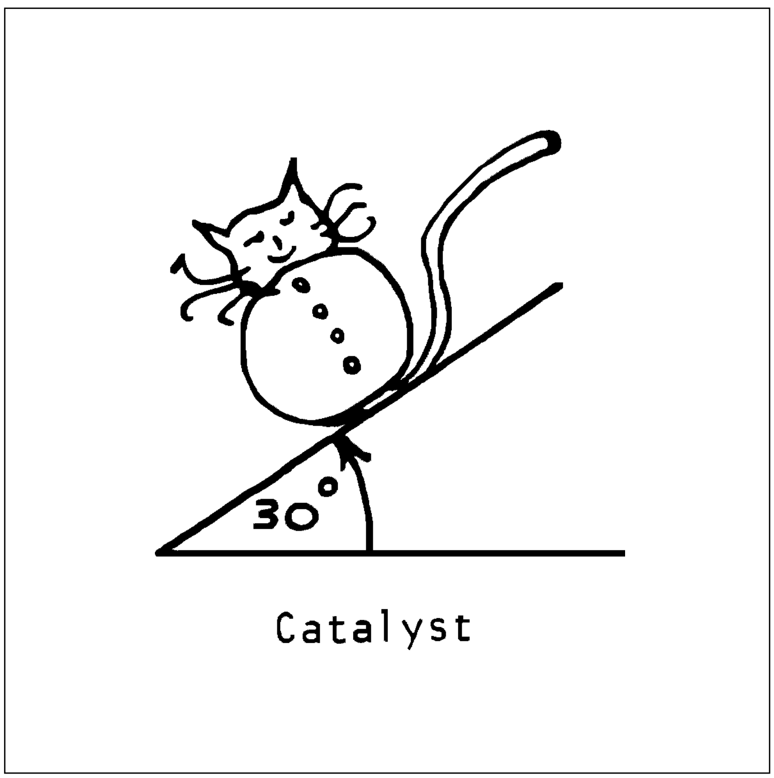

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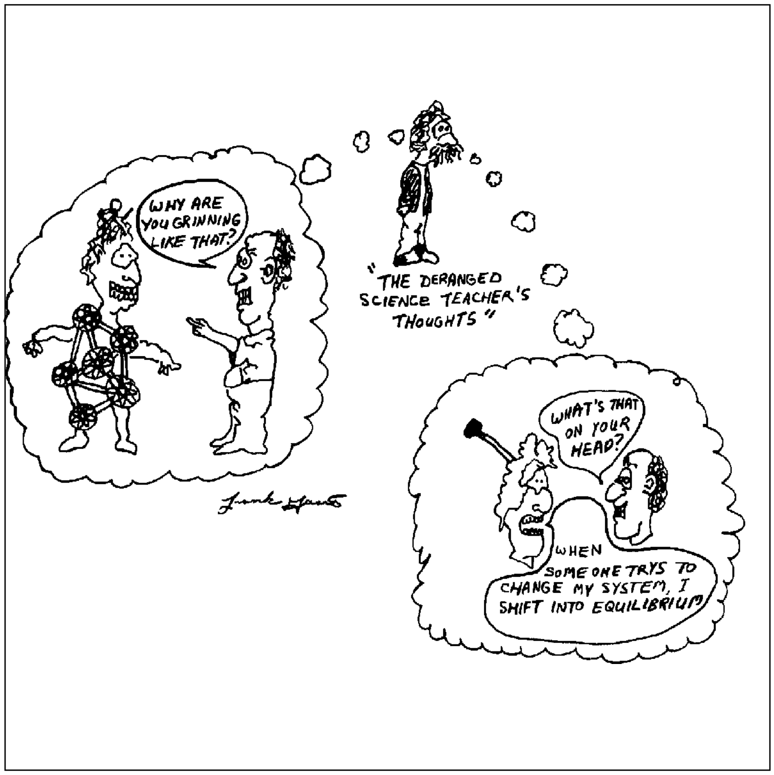

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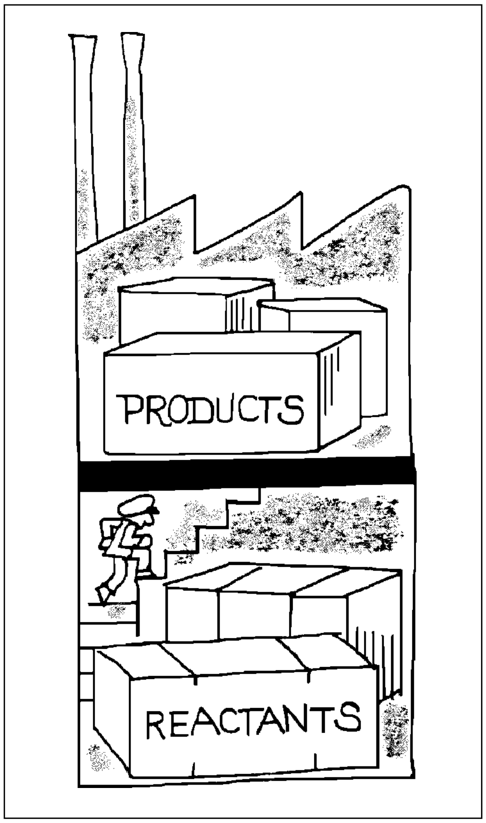

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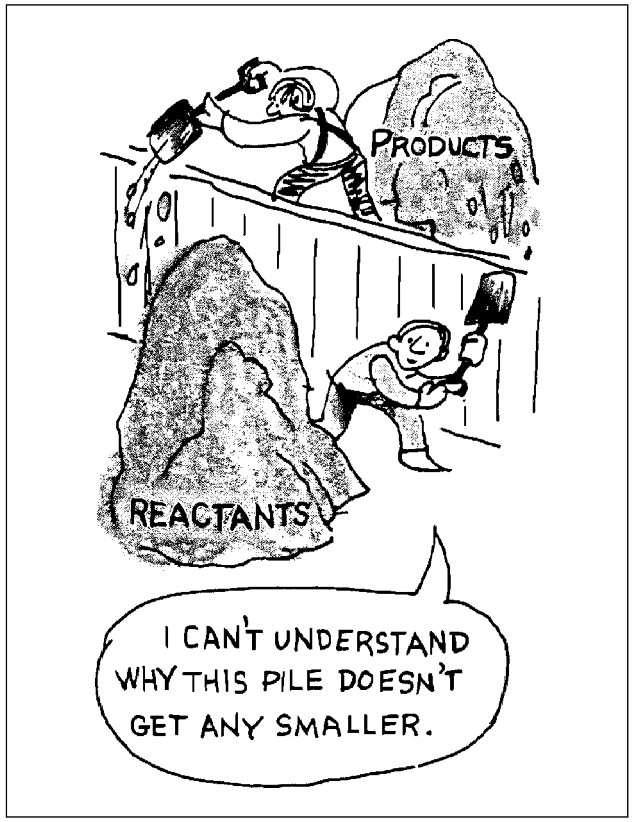

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